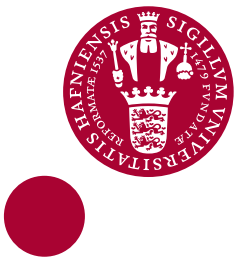

# Redetermination and new description of the crystal structure of vanthoffite, Na6Mg(SO4)4

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# Redetermination and new description of the crystal structure of vanthoffite, $Na_6Mg(SO_4)_4$

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The crystal structure of vanthoffite {hexasodium magnesium tetrakis-[sulfate(VI)]}, $Na_6Mg(SO_4)_4$, was solved in the year 1964 on a synthetic sample [Fischer & Hellner (1964). *Acta Cryst.* **17**, 1613]. Here we report a redetermination of its crystal structure on a mineral sample with improved precision. It was refined in the space group $P2_1/c$ from a crystal originating from Surtsey, Iceland. The unique Mg (site symmetry $\overline{1}$) and the two S atoms are in usual, only slightly distorted octahedral and tetrahedral coordinations, respectively. The three independent Na atoms are in a distorted octahedral coordination (1×) and distorted 7-coordinations intermediate between a 'split octahedron' and a pentagonal bipyramid (2×). [$MgO_6$] coordination polyhedra interchange with one half of the sulfate tetrahedra in <011> chains forming a (100) meshed layer, with dimers formed by edge-sharing [$NaO_7$] polyhedra filling the interchain spaces. The other [$NaO_7$] polyhedra are organized in a parallel layer formed by [010] and [001] chains united through edge sharing and bonds to the remaining half of sulfate groups and to [$NaO_6$] octahedra. The two types of layers interconnect through tight bonding, which explains the lack of morphological characteristics typical of layered structures.

## 1. Chemical context

Vanthoffite is an evaporitic mineral that occurs worldwide in various salt, potash and sulfate marine deposits. It is also reported from the fumaroles of Kamchatka (Pekov *et al.*, 2015) and Iceland (Balić-Žunić *et al.*, 2016). Fischer & Hellner (1964) solved its crystal structure giving the crystal lattice parameters, space group and atomic coordinates with isotropic atomic displacement parameters. To the best of our knowledge the only other crystal structure determination and refinement of an isostructural compound is for $Na_6Mn(SO_4)_4$ (Sharma *et al.*, 2017).

Here we report a redetermination and refinement of the crystal structure of vanthoffite, complete with anisotropic displacement parameters and provide a more detailed description. The precision of the present results is significantly better compared to the previous data of Fischer & Hellner (1964) because of the capabilities of modern X-ray diffraction equipment based on a hybrid photon-counting detector. The obtained *R* factor for the observed reflection data is 3.2% compared to 6.4% for the previous refinement, and the standard deviations of the atomic coordinates and displacement parameters are three to five times smaller. Consequently, the standard deviations of bond lengths and angles are generally ten or more times smaller than previously reported. Comparing our results with those of Fischer & Hellner (1964), we conclude that no differences of substantial character can be observed, and this pays a special credit to the latter work done

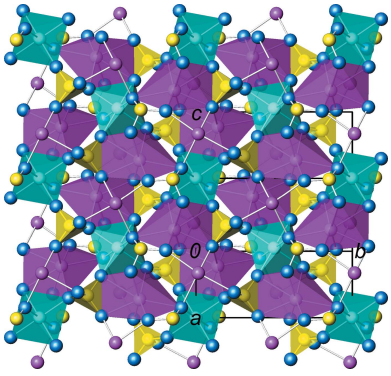

**Table 1**
The parameters of the coordination polyhedra calculated with the program *IVTON* (Balić-Žunić & Vicković, 1996).

| Cation | CN | <d> (Å) | bvs | Vp (Å$^3$) | vd | asp | ecc |
|---|---|---|---|---|---|---|---|
| S1 | 4 | 1.474 | 6.002 | 1.643 (4) | 0.0003 | 0 | 0.0115 |
| S2 | 4 | 1.473 | 6.027 | 1.637 (4) | 0.0006 | 0 | 0.0124 |
| Mg | 6 | 2.083 | 2.094 | 11.99 (2) | 0.0046 | 0.0060 | 0 |
| Na1 | 6 | 2.408 | 1.177 | 17.18 (2) | 0.0716 | 0.0119 | 0.0392 |
| Na2 | 7 | 2.561 | 1.074 | 24.64 (4) | 0.0674 | 0.0586 | 0.0480 |
| Na3 | 7 | 2.524 | 1.071 | 22.76 (3) | 0.0957 | 0.0602 | 0.1492 |

Notes: CN = coordination number; <*d*> = average bond length; bvs = bond valence sum, calculated using the exponential function of Brown & Altermatt (1985) with the parameters of Brese & O'Keeffe (1991); *V*p = polyhedral volume; vd = volume distortion; asp = asphericity; ecc = eccentricity.

with significantly more effort than needed for the present one. The improvement in precision that we obtained, however, allows us to evaluate important structural details that were until now lacking for vanthoffite.

## 2. Structural commentary

In this work, we use three distortion parameters for the description of deviations of atomic coordinations from an ideal geometrical arrangement, *viz.* asphericity, eccentricity and volume distortion, as defined by Balić-Žunić & Makovicky (1996), and Makovicky & Balić-Žunić (1998). Numerical values of these parameters are collated in Table 1. They are useful because they clearly define the type and reason for distortion (in the case of a Jahn–Teller effect or the presence of lone electron pairs), and at the same time define the closest type of the coordination polyhedron.

### 2.1. Coordination polyhedra of Mg and S atoms

The unique Mg atom is located on a symmetry centre and is octahedrally coordinated by O atoms, whereas the two independent S atoms form tetrahedral sulfate groups with oxygen atoms (Fig. 1). The coordinations of Mg and S show very small distortions from the ideal octahedral and tetrahedral arrangements, respectively. As can be seen from Table 1, both S coordination polyhedra have very similar parameters. They are slightly eccentric; the longest bonds are to the O atoms that they share with Mg. This is plausible, because Mg has a larger electronegativity and a higher charge than Na. The Mg coordination polyhedron is even less distorted than those of S. The eccentricity is zero, in accordance with the site being on a symmetry centre and the other two distortion parameters are very low. The anisotropy of the displacement parameters of oxygen atoms bonded to S and Mg, with the overall oblate character of their ellipsoids and the longest diameters approximately perpendicular to the bonding directions, suggests, together with a low anisotropy of S and Mg displacement parameters, a rotational displacement of the coordination polyhedra around their centres (Fig. 1). Each of the vertices of an [$MgO_6$] octahedron is shared with one sulfate tetrahedron, in an arrangement known as a pinwheel structure (Moore, 1973).

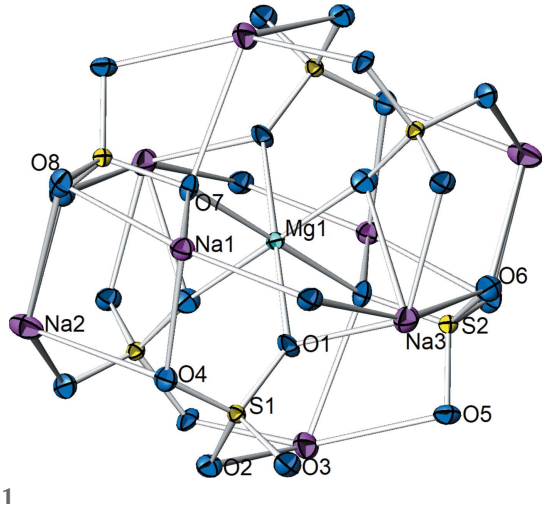


**Figure 1**
The atomic grouping around the [$MgO_6$] coordination polyhedron. Anisotropic displacement ellipsoids are drawn at the 50% probability level.

### 2.2. Coordination polyhedra of Na atoms

The coordination environment for Na atoms is distorted octahedral in the case of Na1 and split-octahedral with a

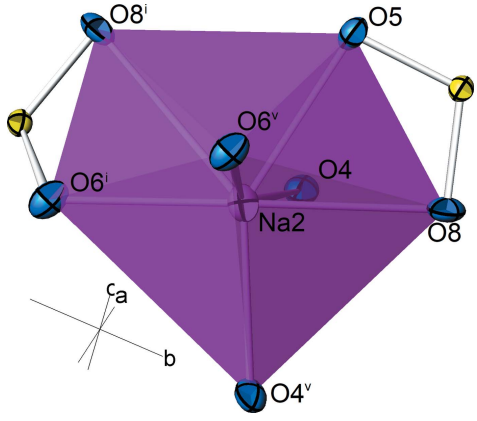


**Figure 2**
Atomic coordination of the Na2 atom. Displacement ellipsoids are as in Fig. 1. [Symmetry codes: (i) $1-x, -\frac{1}{2}+y, \frac{1}{2}-z$; (v) $x, \frac{1}{2}-y, -\frac{1}{2}+z$].

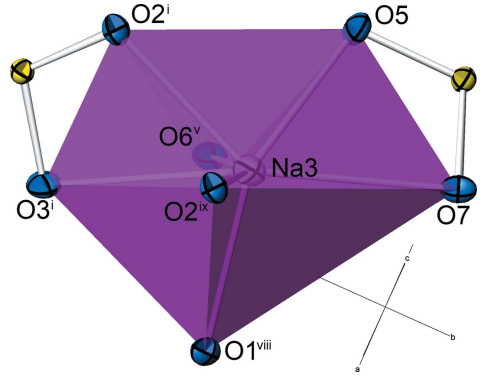


**Figure 3**
Atomic coordination of the Na3 atom. Displacement ellipsoids are as in Fig. 1. [Symmetry codes: (i) $1-x, -\frac{1}{2}+y, \frac{1}{2}-z$; (v) $x, \frac{1}{2}-y, -\frac{1}{2}+z$; (viii) $1+x, y, z$; (ix) $1+x, \frac{1}{2}-y, \frac{1}{2}+z$].

coordination number (CN) of 7 for the other two independent Na sites (Figs. 2 and 3). We consider only the O atoms closer than 3 Å to be bonded to Na. There are further O atoms in the neighbourhood of Na, listed by Fischer & Hellner (1964), but we note that the distance gap to these additional O atoms is significant and their bonding contribution negligible according to bond-valence calculations. The volume distortions of the coordination polyhedra around Na2 and Na3 lie between those of an ideal pentagonal bipyramid (0) and an ideal 'split octahedron' (0.1333). The latter type of coordination was described in detail by Edenharter (1976) and Makovicky & Balić-Žunić (1998). The coordination polyhedron of Na2 (Fig. 2) can either be described as a pentagonal bipyramid with O4 and O6 as polar vertices, or as a split octahedron with O5 and O8 as a split vertex. Likewise, the coordination polyhedron of Na3 (Fig. 3) can either be described as a distorted pentagonal bipyramid with O2 and O6 as polar vertices, or as a split octahedron with the second O2 and O5 as a split vertex. It can, furthermore, be seen from Figs. 2 and 3 that coordination polyhedra of Na2 and Na3 each share two edges with sulfate tetrahedra. Edges O5–O8 and O6–O8 of [$Na2O_7$] are shared with two [$S2O_4$] tetrahedra, whereas edges O2–O3 and O5–O7 of [$Na3O_7$] are shared with a S1 and a S2 coordination tetrahedron, respectively.

### 2.3. Description of the crystal structure as an arrangement of coordination polyhedra of cations

The crystal structure of vanthoffite can be described as an interchange of two types of layers parallel to {100}, here labelled *A* and *B* (Figs. 4 and 5). Layer *A* is centred on the (0, *y*, *z*) plane and built of coordination polyhedra of Mg, S1 and Na3 (Fig. 6). [$MgO_6$] octahedra share four vertices with four [$S1O_4$] tetrahedra. They form intersecting chains running along the <011> directions. Sharma *et al.* (2017) described the crystal structure of the vanthoffite type as having an infinite two-dimensional framework of Mg coordination polyhedra and sulphate groups in the *bc* plane (which we confirm), but describe this framework as being composed of interconnected chains parallel to [010], which is an obvious mistake, as can be seen from Fig. 6. In layer *A*, [$Na3O_7$] coordination polyhedra are arranged in pairs that share a common edge (O2–O2′). If we consider the coordination polyhedra of Mg and Na3 alone, they form chains parallel to [001] in which the Mg and Na coordination polyhedra also share edges (O1–O3). The chains interconnect through common O7 vertices, belonging to both the Mg and Na3 coordination polyhedra. The [$Na3O_7$] polyhedron also shares its O2–O3 edge with an [$S1O_4$] tetrahedron as mentioned above, plus an O1 vertex with another [$S1O_4$] tetrahedron.

Layer *B* is centred on the (1/2, y, z) plane and built of coordination polyhedra of Na1, Na2 and S2 (Fig. 7). [$Na2O_7$]

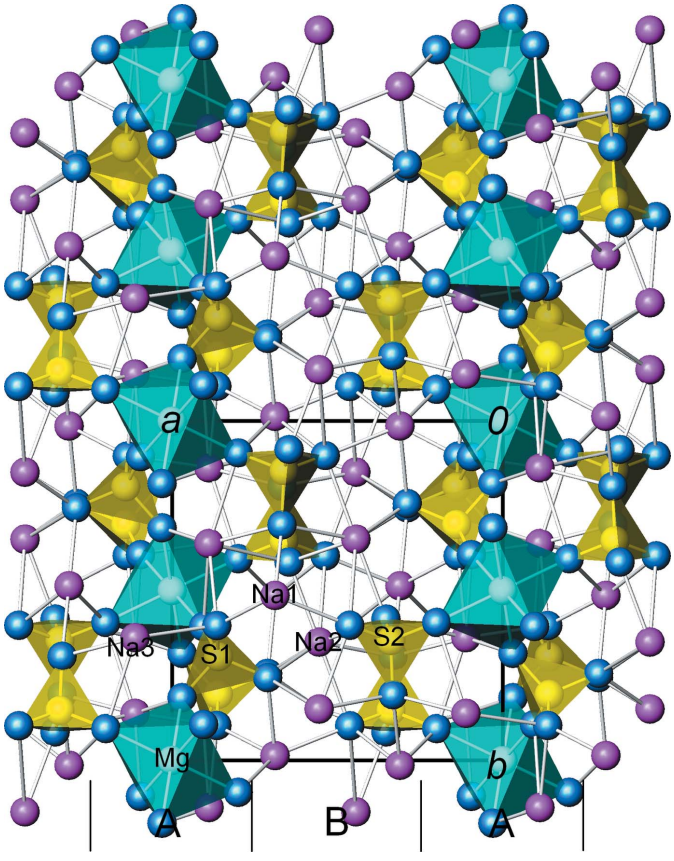


**Figure 4**
Projection of the crystal structure of vanthoffite along [001] with indication of the *A* and *B* structural layers.

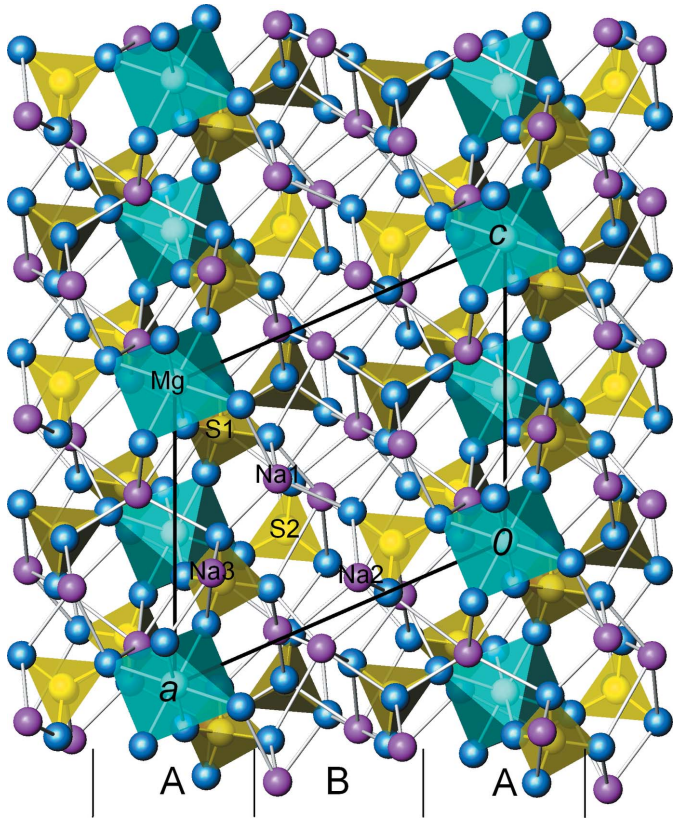


**Figure 5**
Projection of the crystal structure of vanthoffite along [010] with indication of the *A* and *B* structural layers.

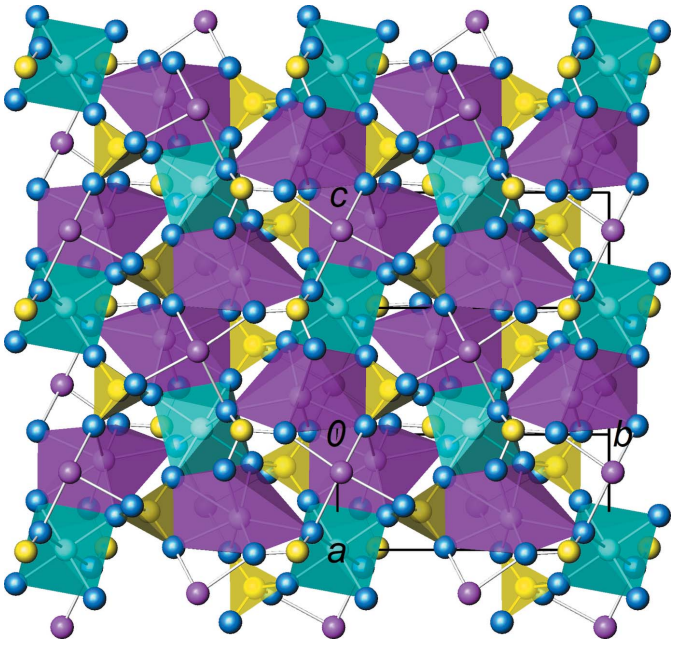


**Figure 6**
Layer *A* formed by the coordination polyhedra of Mg, S1 and Na3, projected on (100), with the *c* axis vertical. Attachment of S2 and Na1, both visualized as spheres, is shown.

coordination polyhedra form chains around the *c* symmetry planes, by sharing O4 vertices. These chains run along [001]. They also form chains along [010] and around $2_1$ axes by sharing O8 vertices. The two types of chains interconnect by sharing O6–O6′ edges, in the middle of which are situated symmetry centres. As mentioned above, [$S2O_4$] tetrahedra, located in this layer, share two edges (O5–O8 and O6–O8)

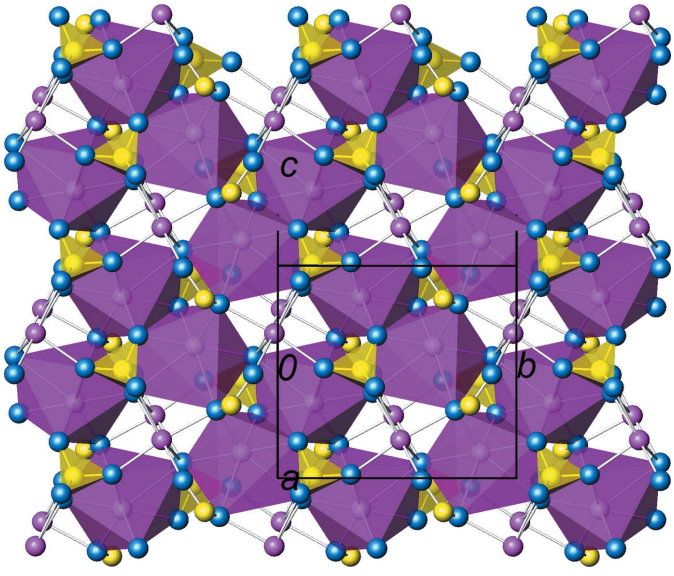


**Figure 7**
Layer *B* formed by the coordination polyhedra of Na1, Na2 and S2, projected on (100), with the *c* axis vertical. To enhance clarity, the coordination polyhedra of Na1 are not filled; attachment of S1 visualized as a sphere is shown.

with [$Na2O_7$] polyhedra. Na1 atoms lie in distorted octahedral holes formed between neighbouring *A* and *B* layers. The corresponding [$Na1O_6$] octahedra share O4–O8 and O5–O8 edges with [$Na2O_7$] and O2–O5 edges with [$Na3O_7$]. There are further interconnections between the two types of layers (O5–O6 edges shared by Na3 and Na2, O5–O7 edges shared by Na3 and S2, plus several shared vertices).

Fischer & Hellner (1964) described the crystal structure of vanthoffite as a distorted hexagonal close packing of sulfate groups, with Mg in $\frac{1}{4}$ of the octahedral holes. The authors did not specify the orientation of the close-packed sulfate layers. There are indeed approximately eutactic layers of sulfate groups parallel to the (001) plane. Their composition and stacking, however, deviate considerably from an ideal eutaxy. Moreover, considering the full framework of coordination polyhedra and chemical bonds, the structure is best described as layered parallel to (100) as in this work and in Hawthorne *et al.* (2000). Most of the previous authors essentially ignored the function of the [$NaO_x$] coordination polyhedra in building the crystal structure, and just mentioned the placement of Na in the holes of the framework of the Mg and S coordination polyhedra. Only Fischer (1973) discussed the three Na coordination types in this structure in a conference abstract. Since Na is the dominating cation in vanthoffite, the structure-building role of the [$NaO_x$] coordination polyhedra also needs to be considered, as we have tried to do in this article.

Vanthoffite is characterized by having six times as many Na atoms as Mg ones. The availability of Na coordination polyhedra in close contact, defining a three-dimensional framework, makes it a potential $Na^+$ ionic conductor. Sharma *et al.* (2017) found a high $Na^+$ conductivity only in the material obtained after the transition of vanthoffite-type $Na_6Mn(SO_4)_4$ to a high-temperature phase. We hope that the present detailed description can help in understanding why $Na^+$ conductivity is observed in the high-temperature form only (once its structure is known), but not in the vanthoffite structure itself.

## 3. Synthesis and crystallization

The crystal used for the crystal structure analysis originates from a sample from Surtsey, collected in 1971 by Dr Svein Peter Jakobsson from the Icelandic Institute of Natural History, four years after the end of eruption that formed this volcanic island. The sample number in the mineral collection of the Institute is IN7484.

## 4. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. Atomic sites were labelled to correspond to the original description of the crystal structure (Fischer & Hellner, 1964). A chemical analysis of the analysed crystal was not performed because of its very small size. As is typical for minerals from volcanic fumaroles, the mineral is fine grained and intimately mixed with several other phases, which makes an accurate chemical analysis extremely difficult,

even on a larger sample. The correspondence of the current crystal-structure parameters to those of the synthetic compound and the results of structural refinement indicate that the chemical composition is indeed very close to ideal without apparent influence from chemical impurities.

## Acknowledgements

We are indebted to the Icelandic Institute of Natural History and the late Dr Svein Peter Jakobsson for providing us with the sample containing vanthoffite crystals.

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**Table 2**
Experimental details.

| | |
|---|---|
| Crystal data | |
| Chemical formula | $Na_6Mg(SO_4)_4$ |
| $M_r$ | 546.5 |
| Crystal system, space group | Monoclinic, $P2_1/c$ |
| Temperature (K) | 296 |
| $a, b, c$ (Å) | 9.7761 (6), 9.1998 (4), 8.2040 (5) |
| $\beta$ (°) | 113.518 (7) |
| $V$ (Å$^3$) | 676.56 (7) |
| $Z$ | 2 |
| Radiation type | Mo $K\alpha$ |
| $\mu$ (mm$^{-1}$) | 1.04 |
| Crystal size (mm) | 0.03 × 0.02 × 0.004 |
| | |
| Data collection | |
| Diffractometer | SuperNova Rigaku Oxford Diffraction diffractometer with Pilatus200K detector |
| Absorption correction | Multi-scan (*CrysAlis PRO*; Rigaku OD, 2019) |
| $T_{min}$, $T_{max}$ | 0.860, 1.000 |
| No. of measured, independent and observed [$I > 3\sigma(I)$] reflections | 18695, 2211, 1432 |
| $R_{int}$ | 0.087 |
| $(\sin\theta/\lambda)_{max}$ (Å$^{-1}$) | 0.744 |
| | |
| Refinement | |
| $R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, $S$ | 0.032, 0.037, 1.29 |
| No. of reflections | 2211 |
| No. of parameters | 124 |
| $\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å$^{-3}$) | 0.61, −0.67 |

Computer programs: *CrysAlis PRO* (Rigaku OD, 2019), *SUPERFLIP* (Oszlányi & Sütő, 2004; Palatinus & Chapuis, 2007), *JANA2006* (Petříček *et al.*, 2014), *ATOMS* (Dowty, 2005).

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# supporting information

*Acta Cryst.* (2020). E**76**, 785-789 [https://doi.org/10.1107/S2056989020005873]

## Redetermination and new description of the crystal structure of vanthoffite, $Na_6Mg(SO_4)_4$

**Tonči Balić-Žunić, Martha G. Pamato and Fabrizio Nestola**

### Computing details

Data collection: *CrysAlis PRO* (Rigaku OD, 2019); cell refinement: *CrysAlis PRO* (Rigaku OD, 2019); data reduction: *CrysAlis PRO* (Rigaku OD, 2019); program(s) used to solve structure: Superflip (Oszlányi & Sütő, 2004; Palatinus & Chapuis, 2007); program(s) used to refine structure: Jana2006 (Petříček *et al.*, 2014); molecular graphics: *ATOMS* (Dowty, 2005).

### Hexasodium magnesium tetrakis[sulfate(VI)]

*Crystal data*

$Na_6Mg(SO_4)_4$
$M_r$ = 546.5
Monoclinic, $P2_1/c$
Hall symbol: -P 2ycb
$a$ = 9.7761 (6) Å
$b$ = 9.1998 (4) Å
$c$ = 8.2040 (5) Å
$\beta$ = 113.518 (7)°
$V$ = 676.56 (7) Å$^3$
$Z$ = 2
$F(000)$ = 540
$D_x$ = 2.682 Mg m$^{-3}$
Mo $K\alpha$ radiation, $\lambda$ = 0.71073 Å
Cell parameters from 3897 reflections
$\theta$ = 2.3–31.7°
$\mu$ = 1.04 mm$^{-1}$
$T$ = 296 K
Plate, colourless
0.03 × 0.02 × 0.004 mm

*Data collection*

SuperNova Rigaku Oxford Diffraction diffractometer with Pilatus200K detector
Radiation source: micro-focus sealed X-ray tube, SuperNova (Mo) X-ray Source
Mirror monochromator
Detector resolution: 5.8140 pixels mm$^{-1}$
$\omega$ scans
Absorption correction: multi-scan (CrysAlisPro; Rigaku OD, 2019)
$T_{min}$ = 0.860, $T_{max}$ = 1.000
18695 measured reflections
2211 independent reflections
1432 reflections with $I > 3\sigma(I)$
$R_{int}$ = 0.087
$\theta_{max}$ = 31.9°, $\theta_{min}$ = 2.3°
$h$ = −14→14
$k$ = −13→13
$l$ = −12→11

*Refinement*

Refinement on $F$
$R[F^2 > 2\sigma(F^2)]$ = 0.032
$wR(F^2)$ = 0.037
$S$ = 1.29
2211 reflections
124 parameters
0 restraints
0 constraints
Weighting scheme based on measured s.u.'s $w = 1/(\sigma^2(F) + 0.0001F^2)$
$(\Delta/\sigma)_{max}$ = 0.047
$\Delta\rho_{max}$ = 0.61 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.67 e Å$^{-3}$

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)*

| | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| S1 | 0.14002 (6) | 0.30539 (6) | 0.22425 (8) | 0.01023 (19) |
| S2 | 0.66143 (6) | 0.35283 (6) | 0.34685 (8) | 0.01116 (19) |
| Mg1 | 0 | 0 | 0 | 0.0097 (4) |
| Na1 | 0.31120 (11) | 0.01426 (11) | 0.46772 (12) | 0.0173 (4) |
| Na2 | 0.44443 (12) | 0.15141 (12) | 0.09037 (14) | 0.0262 (4) |
| Na3 | 0.88822 (12) | 0.13860 (11) | 0.31627 (14) | 0.0231 (4) |
| O1 | 0.03029 (18) | 0.18470 (18) | 0.1553 (2) | 0.0153 (6) |
| O2 | 0.13531 (19) | 0.39708 (19) | 0.0752 (2) | 0.0169 (6) |
| O3 | 0.0954 (2) | 0.39427 (19) | 0.3441 (2) | 0.0197 (7) |
| O4 | 0.28894 (18) | 0.24382 (19) | 0.3187 (2) | 0.0198 (7) |
| O5 | 0.66765 (19) | 0.19352 (18) | 0.3593 (2) | 0.0175 (6) |
| O6 | 0.6464 (2) | 0.4160 (2) | 0.5023 (2) | 0.0208 (7) |
| O7 | 0.80007 (17) | 0.40614 (19) | 0.3324 (2) | 0.0154 (6) |
| O8 | 0.53693 (18) | 0.39792 (19) | 0.1825 (2) | 0.0190 (6) |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| S1 | 0.0103 (3) | 0.0099 (3) | 0.0103 (3) | −0.0010 (2) | 0.0039 (2) | −0.0008 (2) |
| S2 | 0.0109 (3) | 0.0099 (3) | 0.0126 (3) | 0.0001 (2) | 0.0046 (2) | 0.0006 (2) |
| Mg1 | 0.0096 (5) | 0.0090 (6) | 0.0101 (5) | 0.0002 (4) | 0.0034 (4) | −0.0002 (4) |
| Na1 | 0.0195 (5) | 0.0154 (5) | 0.0181 (5) | −0.0002 (4) | 0.0088 (4) | 0.0005 (4) |
| Na2 | 0.0266 (6) | 0.0187 (6) | 0.0259 (6) | −0.0064 (4) | 0.0026 (5) | −0.0002 (5) |
| Na3 | 0.0257 (6) | 0.0206 (6) | 0.0305 (6) | 0.0040 (4) | 0.0190 (5) | 0.0039 (5) |
| O1 | 0.0156 (8) | 0.0149 (9) | 0.0167 (9) | −0.0076 (7) | 0.0077 (7) | −0.0072 (7) |
| O2 | 0.0222 (9) | 0.0155 (9) | 0.0159 (9) | 0.0009 (7) | 0.0105 (7) | 0.0041 (7) |
| O3 | 0.0267 (10) | 0.0184 (10) | 0.0189 (10) | −0.0037 (8) | 0.0145 (8) | −0.0073 (8) |
| O4 | 0.0118 (8) | 0.0182 (10) | 0.0251 (10) | 0.0011 (7) | 0.0028 (7) | 0.0031 (8) |
| O5 | 0.0223 (9) | 0.0111 (9) | 0.0195 (9) | 0.0010 (7) | 0.0088 (7) | 0.0027 (7) |
| O6 | 0.0270 (10) | 0.0198 (10) | 0.0219 (10) | −0.0028 (8) | 0.0165 (8) | −0.0052 (8) |
| O7 | 0.0095 (8) | 0.0208 (9) | 0.0144 (9) | −0.0026 (7) | 0.0031 (7) | 0.0005 (7) |
| O8 | 0.0113 (8) | 0.0231 (10) | 0.0174 (9) | 0.0007 (7) | 0.0003 (7) | 0.0061 (8) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| S1—O1 | 1.4897 (17) | Na1—O8$^{i}$ | 2.516 (2) |
| S1—O2 | 1.4710 (19) | Na1—O8$^{vii}$ | 2.3504 (17) |
| S1—O3 | 1.472 (2) | Na1—O4 | 2.406 (2) |
| S1—O4 | 1.4630 (16) | Na3—O7 | 2.628 (2) |
| S2—O7 | 1.490 (2) | Na3—O1$^{viii}$ | 2.305 (2) |
| S2—O5 | 1.4687 (18) | Na3—O5 | 2.374 (2) |
| S2—O8 | 1.4703 (15) | Na3—O2$^{i}$ | 2.438 (2) |
| S2—O6 | 1.461 (2) | Na3—O2$^{ix}$ | 2.5219 (18) |
| Mg1—O7$^{i}$ | 2.0765 (15) | Na3—O3$^{i}$ | 2.641 (2) |
| Mg1—O7$^{ii}$ | 2.0765 (15) | Na3—O6$^{v}$ | 2.7595 (18) |

| | | | |
|---|---|---|---|
| Mg1—O1 | 2.0732 (17) | Na2—O5 | 2.4368 (18) |
| Mg1—O1$^{iii}$ | 2.0732 (17) | Na2—O8 | 2.447 (2) |
| Mg1—O3$^{iv}$ | 2.099 (2) | Na2—O8$^{i}$ | 2.945 (2) |
| Mg1—O3$^{v}$ | 2.099 (2) | Na2—O4 | 2.969 (3) |
| Na1—O7$^{i}$ | 2.4691 (19) | Na2—O4$^{v}$ | 2.3460 (19) |
| Na1—O5$^{vi}$ | 2.340 (2) | Na2—O6$^{i}$ | 2.349 (2) |
| Na1—O2$^{vii}$ | 2.369 (2) | Na2—O6$^{v}$ | 2.438 (3) |

| | | | |
|---|---|---|---|
| O1—S1—O2 | 109.45 (9) | O7—Na3—O1$^{viii}$ | 98.11 (7) |
| O1—S1—O3 | 107.87 (11) | O7—Na3—O5 | 57.17 (6) |
| O1—S1—O4 | 109.04 (10) | O7—Na3—O2$^{i}$ | 138.97 (9) |
| O2—S1—O3 | 108.49 (11) | O7—Na3—O2$^{ix}$ | 107.61 (6) |
| O2—S1—O4 | 110.90 (12) | O7—Na3—O3$^{i}$ | 155.25 (6) |
| O3—S1—O4 | 111.03 (10) | O7—Na3—O6$^{v}$ | 92.37 (6) |
| O7—S2—O5 | 108.68 (11) | O1$^{viii}$—Na3—O5 | 146.76 (7) |
| O7—S2—O8 | 106.29 (11) | O1$^{viii}$—Na3—O2$^{i}$ | 122.88 (8) |
| O7—S2—O6 | 110.50 (11) | O1$^{viii}$—Na3—O2$^{ix}$ | 85.01 (7) |
| O5—S2—O8 | 109.97 (9) | O1$^{viii}$—Na3—O3$^{i}$ | 72.61 (7) |
| O5—S2—O6 | 110.59 (11) | O1$^{viii}$—Na3—O6$^{v}$ | 89.22 (7) |
| O8—S2—O6 | 110.70 (11) | O5—Na3—O2$^{i}$ | 85.18 (7) |
| O7$^{i}$—Mg1—O7$^{ii}$ | 180 | O5—Na3—O2$^{ix}$ | 121.59 (8) |
| O7$^{i}$—Mg1—O1 | 93.89 (6) | O5—Na3—O3$^{i}$ | 119.63 (7) |
| O7$^{i}$—Mg1—O1$^{iii}$ | 86.11 (6) | O5—Na3—O6$^{v}$ | 71.75 (7) |
| O7$^{i}$—Mg1—O3$^{iv}$ | 86.17 (7) | O2$^{i}$—Na3—O2$^{ix}$ | 76.82 (6) |
| O7$^{i}$—Mg1—O3$^{v}$ | 93.83 (7) | O2$^{i}$—Na3—O3$^{i}$ | 55.92 (7) |
| O7$^{ii}$—Mg1—O1 | 86.11 (6) | O2$^{i}$—Na3—O6$^{v}$ | 90.26 (6) |
| O7$^{ii}$—Mg1—O1$^{iii}$ | 93.89 (6) | O2$^{ix}$—Na3—O3$^{i}$ | 94.63 (6) |
| O7$^{ii}$—Mg1—O3$^{iv}$ | 93.83 (7) | O2$^{ix}$—Na3—O6$^{v}$ | 159.78 (7) |
| O7$^{ii}$—Mg1—O3$^{v}$ | 86.17 (7) | O3$^{i}$—Na3—O6$^{v}$ | 65.16 (6) |
| O1—Mg1—O1$^{iii}$ | 180 | O5—Na2—O8 | 59.06 (6) |
| O1—Mg1—O3$^{iv}$ | 89.68 (7) | O5—Na2—O8$^{i}$ | 75.29 (6) |
| O1—Mg1—O3$^{v}$ | 90.32 (7) | O5—Na2—O4 | 83.23 (7) |
| O1$^{iii}$—Mg1—O3$^{iv}$ | 90.32 (7) | O5—Na2—O4$^{v}$ | 143.28 (8) |
| O1$^{iii}$—Mg1—O3$^{v}$ | 89.68 (7) | O5—Na2—O6$^{i}$ | 121.73 (7) |
| O3$^{iv}$—Mg1—O3$^{v}$ | 180 | O5—Na2—O6$^{v}$ | 76.71 (7) |
| O7$^{i}$—Na1—O5$^{vi}$ | 99.95 (7) | O8—Na2—O8$^{i}$ | 128.07 (7) |
| O7$^{i}$—Na1—O2$^{vii}$ | 114.43 (7) | O8—Na2—O4 | 76.04 (7) |
| O7$^{i}$—Na1—O8$^{i}$ | 56.73 (6) | O8—Na2—O4$^{v}$ | 86.11 (6) |
| O7$^{i}$—Na1—O8$^{vii}$ | 142.59 (9) | O8—Na2—O6$^{i}$ | 179.16 (7) |
| O7$^{i}$—Na1—O4 | 86.12 (7) | O8—Na2—O6$^{v}$ | 94.82 (8) |
| O5$^{vi}$—Na1—O2$^{vii}$ | 87.54 (8) | O8$^{i}$—Na2—O4 | 75.26 (6) |
| O5$^{vi}$—Na1—O8$^{i}$ | 91.31 (7) | O8$^{i}$—Na2—O4$^{v}$ | 141.22 (7) |
| O5$^{vi}$—Na1—O8$^{vii}$ | 89.82 (6) | O8$^{i}$—Na2—O6$^{i}$ | 52.75 (6) |
| O5$^{vi}$—Na1—O4 | 173.33 (8) | O8$^{i}$—Na2—O6$^{v}$ | 97.65 (7) |
| O2$^{vii}$—Na1—O8$^{i}$ | 170.73 (6) | O4—Na2—O4$^{v}$ | 100.43 (7) |
| O2$^{vii}$—Na1—O8$^{vii}$ | 101.91 (7) | O4—Na2—O6$^{i}$ | 104.22 (8) |
| O2$^{vii}$—Na1—O4 | 87.42 (7) | O4—Na2—O6$^{v}$ | 159.86 (6) |
| O8$^{i}$—Na1—O8$^{vii}$ | 87.27 (7) | O4$^{v}$—Na2—O6$^{i}$ | 93.06 (7) |

| | | | |
|---|---|---|---|
| O8$^{i}$—Na1—O4 | 94.35 (8) | O4$^{v}$—Na2—O6$^{v}$ | 96.74 (8) |
| O8$^{vii}$—Na1—O4 | 86.94 (6) | O6$^{i}$—Na2—O6$^{v}$ | 85.18 (8) |

Symmetry codes: (i) −*x*+1, *y*−1/2, −*z*+1/2; (ii) *x*−1, −*y*+1/2, *z*−1/2; (iii) −*x*, −*y*, −*z*; (iv) −*x*, *y*−1/2, −*z*+1/2; (v) *x*, −*y*+1/2, *z*−1/2; (vi) −*x*+1, −*y*, −*z*+1; (vii) *x*, −*y*+1/2, *z*+1/2; (viii) *x*+1, *y*, *z*; (ix) *x*+1, −*y*+1/2, *z*+1/2.